High Performance non-PGM Transition Metal Oxide ORR Catalysts of PEMFCs

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United Technologies Research Center

ElectroCat Consortia Project

Project ID: **FC306**

DE-EE0008420

April 29, 2019

Overview

Timeline

Project Start: March 2019

Project Q1: March-May 2019

Project End: February 2021

24 months

Key Barriers

- Achieve DOE's 2020 Targets for non-PGM MEAs

Target I.D. #	Characteristic	Units	2020 Targets
FC 4	Loss in initial catalytic activity	% mass loss	< 40
FC 5	Loss in performance at 0.8 A cm^{-2}	mV	< 30
FC 8	PGM-free catalyst activity	A cm^{-2} at 900 $mV_{iR\text{-}free}$	> 0.044

Budget

Total Project Budget: $1,250K

- Federal Share $1,000K
- Cost Share (20%) $250K

Total DOE Funds Spent*: **$41K**

*** as of 3/11/2017**

Partners

Massachusetts Institute of Technology

ElectroCat Electrocatalysis Consortium

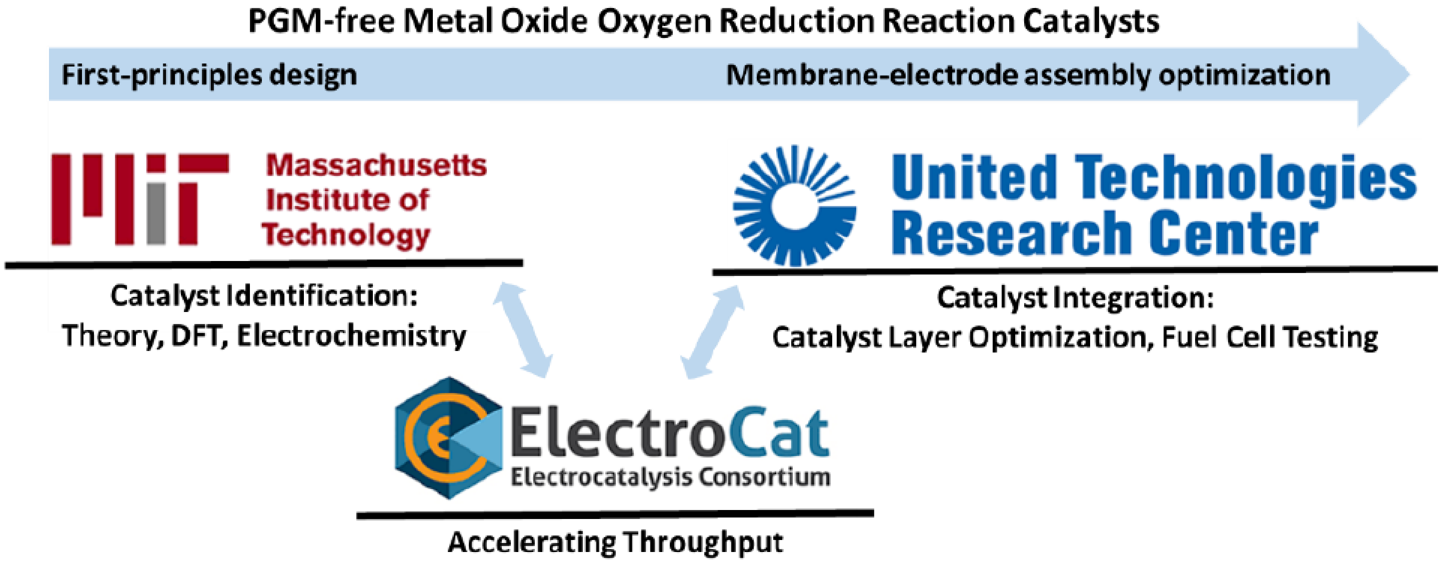
Relevance

Objective: Develop *acid-stable non-PGM metal oxides* and *optimize oxide catalytic activity for ORR reactivity.*

- Utilize high-throughput computational methods to develop acid-stable complex doped transition metal oxides
  - Survey materials complex and/or nonstoichiometric molecular formulae
- Leverage high-throughput experimental electrochemical testing to optimize identified acid-stable oxides for ORR electrocatalytic activity
- Utilize a rapid development process to optimize ink formulation and optimize MEA fabrication for metal oxide electrocatalysts

Project Approach

Roles of key participants



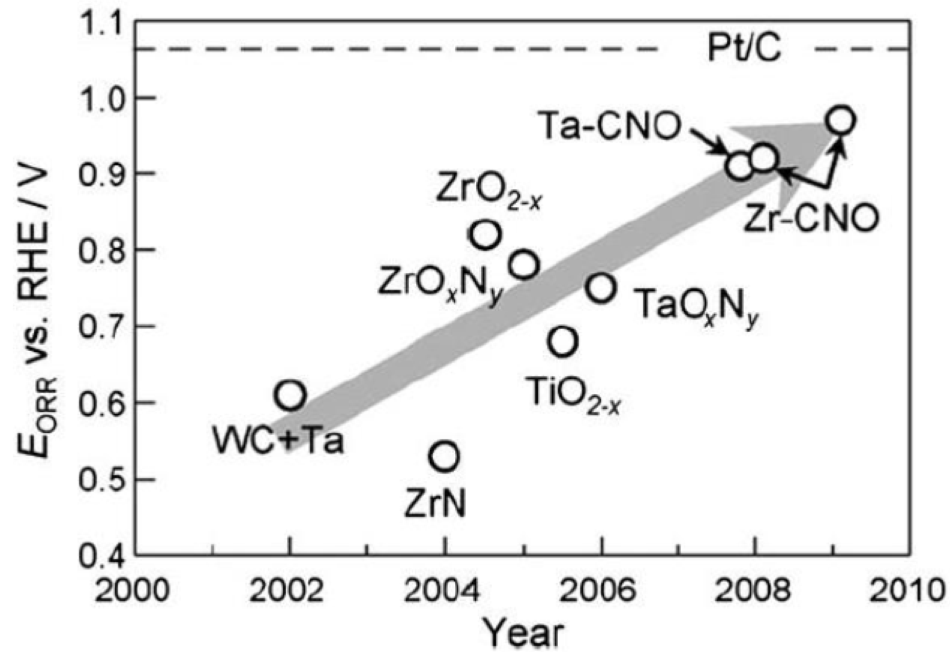
MIT and UTRC have the capabilities to perform project work

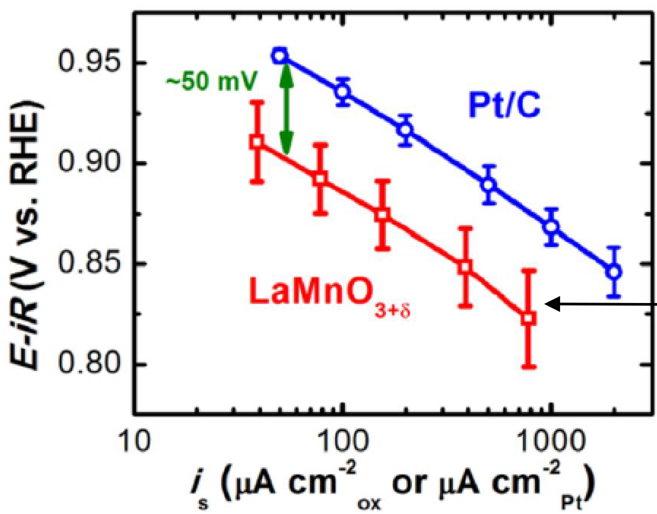
ElectroCat can provide additional high-throughput capabilities to greatly increase the number of materials that can be analyzed to meet the aggressive timetable

Technical Approach

Metal oxide ORR PEM catalysts

- Current research in non-PGM catalysis is primarily MNC-type catalysts
- Metal oxides have been studied but focused primarily on group IV/V due to acid stability
  - To date, oxide ORR catalysts are generally poor





Transition metal oxides can be good ORR catalysts in alkaline conditions

- The activity of $LaMnO_{3-\delta}$ is suitable for fuel cell applications

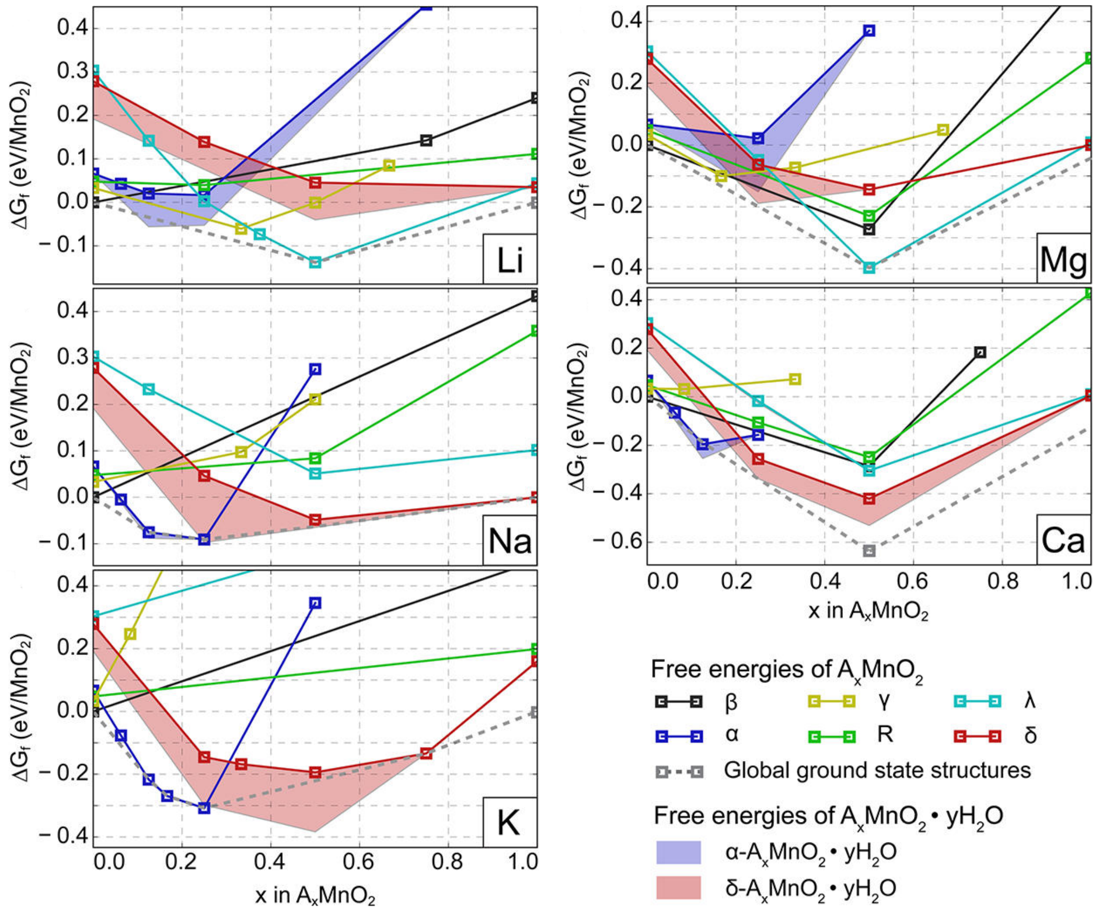
Chen, *et al.*, *Energy Environ. Sci.*, **2011**, *4*, 3167
Suntivich, **Shao-Horn**, *et al.*, *Nature Chem.*, **2011**, *3*, 546

Technical Approach

There is little data on Mn/Fe/Co oxide ORR performance in acidic conditions. Oxides with these metals are expected to be more catalytically active.

- The acid solubility of Mn/Fe/Co oxides is poor
- Stability of oxides can be improved by the addition of dopants

If acid-stable oxide frameworks are found that include catalytically active elements, there is the potential for a breakthrough in oxide ORR performance



Kitchaev, *et al.*, *J. Am. Chem. Soc.*, **2017**, *139*, 2672

Approach: Milestones Progress

Milestone I.D. Number	Task #s	Milestone Task or Title	Milestone Description (Detailed Go/No Go Criteria are described in Table III below)	Delivery Date	Complete
M1	1	Program Management	Subcontract completed	6/1/19	
M2	2	Evaluation of acid stability of A_xMnO_2 and/or doped $Cu_{1.5}Mn_{1.5}O_4$	Experimentally verify stability of A_xMnO_2 (A = alkali or alkaline earth element) and/or doped $Cu_{1.5}Mn_{1.5}O_4$	6/1/19	5%
M3	3	Evaluation of intrinsic ORR activity of acid-Stable A_xMnO_2 and/or doped $Cu_{1.5}Mn_{1.5}O_4$	Experimentally determine intrinsic ORR activity of acid-stable A_xMnO_2 and/or doped $Cu_{1.5}Mn_{1.5}O_4$	9/1/19	0%
M4	2	Evaluation of acid stability of 2nd generation oxides	Computational prediction of acid-stable oxides and experimental verification of acid stability of 2nd generation oxides	9/1/19	0%
M5		Optimize catalyst layer composition with best A_xMnO_2 catalyst or doped $Cu_{1.5}Mn_{1.5}O_4$	Optimize catalyst particle size and catalyst/carbon/ionomer composition and demonstrate capability to create catalyst particles with surface area ≥ 100 m^2-g^{-1}	12/1/19	0%
M6	3	Evaluation of intrinsic ORR activity of 2nd generation oxides	Experimentally determine intrinsic ORR activity of 2nd generation oxides (one of these materials should be predicted to meet first year MEA requirements)	12/1/19	0%
M7	2	Evaluation of acid stability of 3rd generation oxides	Computational prediction of acid-stable oxides and experimental verification of acid stability of 3rd generation oxides using lessons learned from 2nd generation	12/1/19	0%
M8 1 Go/No Go	3	Evaluation of intrinsic ORR activity of 3rd generation oxides	Demonstrate intrinsic ORR activity ≥ 4.4 μA-cm^{-2} at 0.9 V (iR-free) under 1 atm O_2 with an acid stable oxide where acid stability is demonstrated by < 10% performance loss after 100 hours measured according to the RDE electrochemical durability test.	3/1/20	0%
M9 2 Go/No Go					0%

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Approved for Public Release

Accomplishments & Progress

- Contract negotiations ongoing as of 3/11/19
- Held kick-off meeting with MIT
- Scheduled site visit to MIT for 3/15/19
- Presented at ElectroCat consortium meeting in Santa Fe 1/30 – 2/1/19

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Massachusetts Institute of Technology

- Begun to engage ElectroCat Consortium members
  - Focus on high-throughput electrochemical characterization and testing

ElectroCat Electrocatalysis Consortium

UTRC has begun working on the project at risk

Responses to Reviewer's Comments

- This project was not reviewed last year.

Collaborations

Core Project Team

First principles design to membrane-electrode assembly

Subcontractor, University

Massachusetts Institute of Technology

- Oxide optimization for acid stability
- ORR Electrocatalytic performance optimization of acid-stable oxides

Yang Shao-Horn

Prime, Industry

United Technologies Research Center

- Catalyst Layer Optimization
- MEA Fabrication
- MEA Performance and Durability Testing

Tim Davenport (Project, Experimental)
Mike Perry (Project)
Rob Darling (Transport Modeling)

Core team has capability to lead modeling and fabricate key materials required

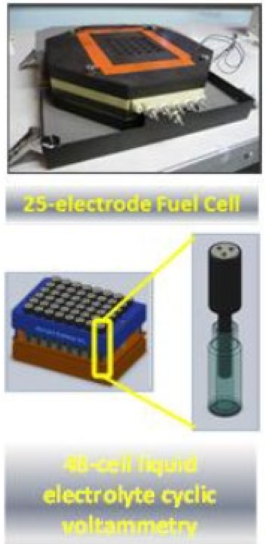
Collaborations

ElectroCat Consortium Engagement

- Primary capabilities that will be pursued are high-throughput methods
- Extent of collaboration will be defined when samples are ready for testing

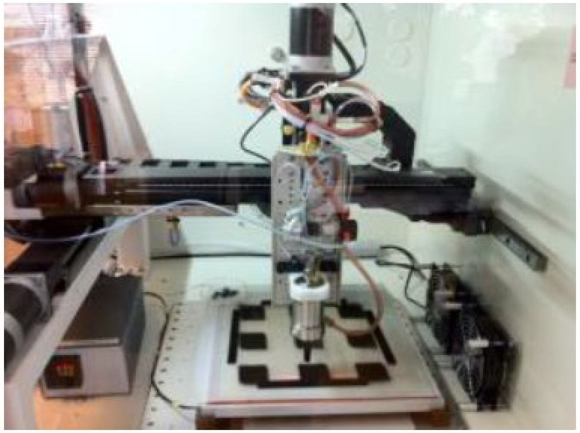
Highest Priority Capabilities

- High-throughput electrochemical testing
- High-throughput electrode fabrication
- High-throughput electrode layer optimization



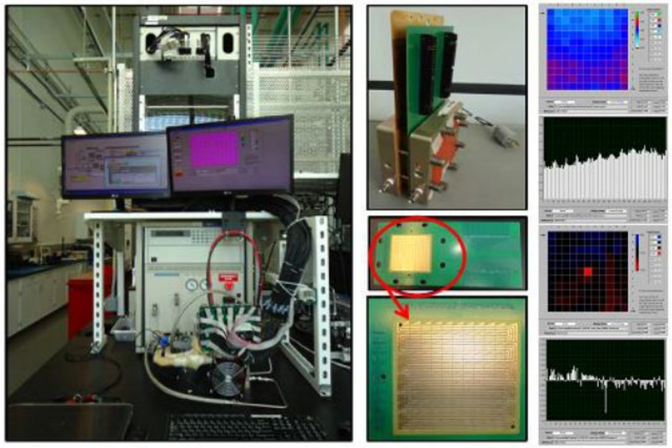
T. Krause, M. Ferrandon, D. Myers ANL

HT E-chem



M. Ulsh NREL

HT electrode fab



G. Bender NREL

HT electrode opt.

Core team has capability to lead modeling and fabricate key materials required

Challenges and Barriers

- **Challenge:** Every subsequent milestone depends on the discovery of the first-generation of acid-stable oxides – successful completion of this milestone cannot be delayed

- **Planned Resolution:** Both MIT and UTRC will work to complete this milestone with parallel approaches. MIT will use computational methods to identify potential acid-stable oxides. UTRC will use an experimental approach to test potential candidate oxides from the literature.

- The speed of completion of other milestones will depend on interaction with ElectroCat, which has the high-throughput testing capabilities.

Proposed Future Work

Major goals for the next year of this project:

- Identify and develop a first generation acid-stable oxide ORR electrocatalyst

Milestone I.D.	Task Title	Brief Milestone Description
3/1/2020 Go/No-Go	Non-PGM Performance Demonstration	Demonstrate MEA with performance of 0.025 A-cm^{-2} at 0.9 V under 1 atm O_2 and 80 °C.

- Achieving this goal will require parallel development paths between MIT and UTRC
  - MIT will use a computational approach to identify acid-stable oxide electrocatalysts and transfer them to UTRC for MEA development
  - UTRC will begin testing F-doped $Cu_{1.5}Mn_{1.5}O_4$ reported to have ideal performance
  - UTRC will also begin preparing acid-stable (or metastable) materials developed for lead acid battery cathodes ($BaPbO_3$, FTO, Magnéli TiO_x) and doping with potential ORR catalyst elements (i.e. Mn)
  - Any promising acid-stable oxide catalyst will be doped and dopants that incorporate nonstoichiometrically will be prepared for high-throughput electrochemical testing of the nonstoichiometric range

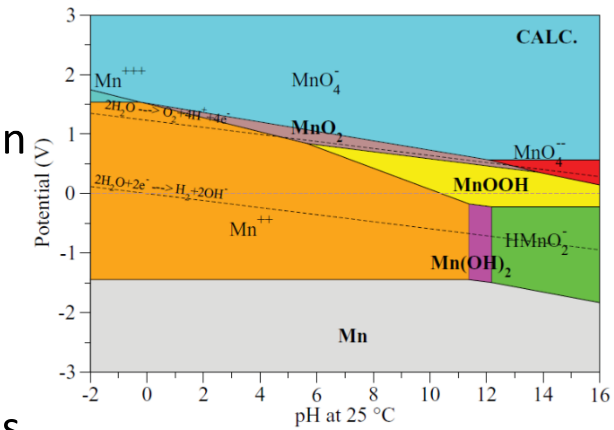
Any proposed future work is subject to change based on funding levels

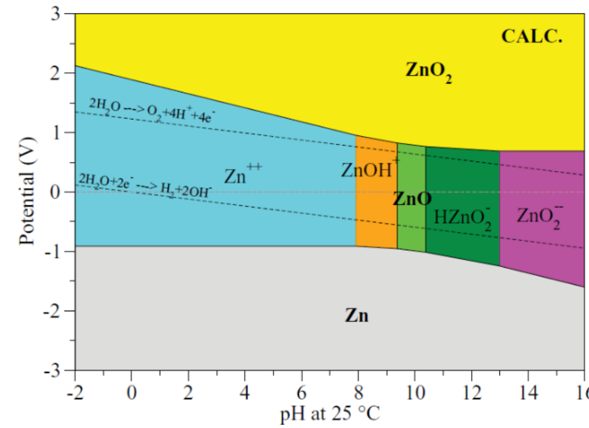
Proposed Future Work

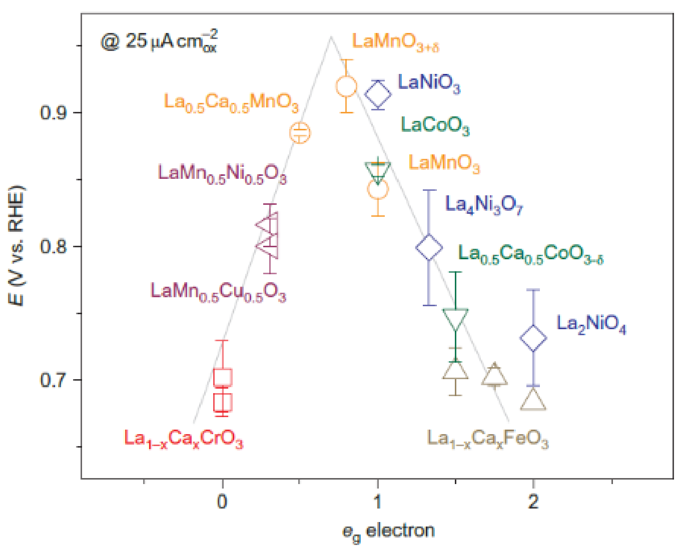
Planned for this year: Acid-stabilization of metal oxide phases (2 approaches)

Approach 1: Computing Pourbaix diagrams

- The Materials Project permits the rapid calculation of Pourbaix diagrams
  - Techniques have been developed to handle metastable compounds







- **Approach 2**: Develop molecular orbital-based acid stability descriptor
  - Analagous to descriptor development for ORR electrocatalyst performance

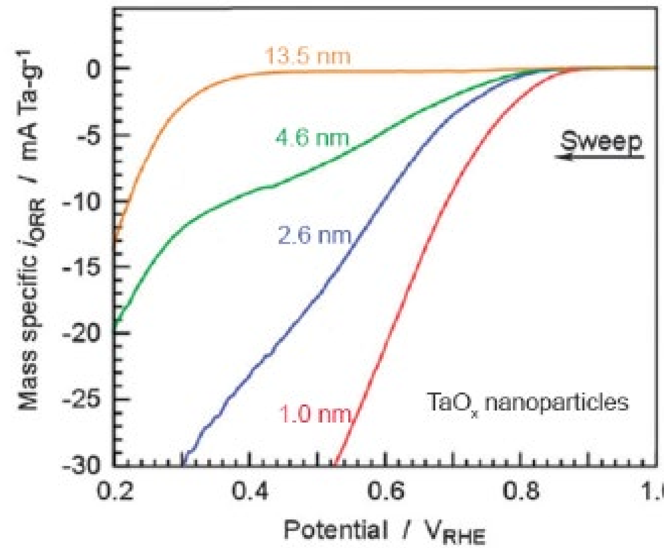
Persson, *et al.*, *Phys. Rev. B*, **2012**, *85*, 235438
Suntivich, **Shao-Horn**, *et al. Nature Chem.* **2011**, *3*, 546

Any proposed future work is subject to change based on funding levels

Proposed Future Work

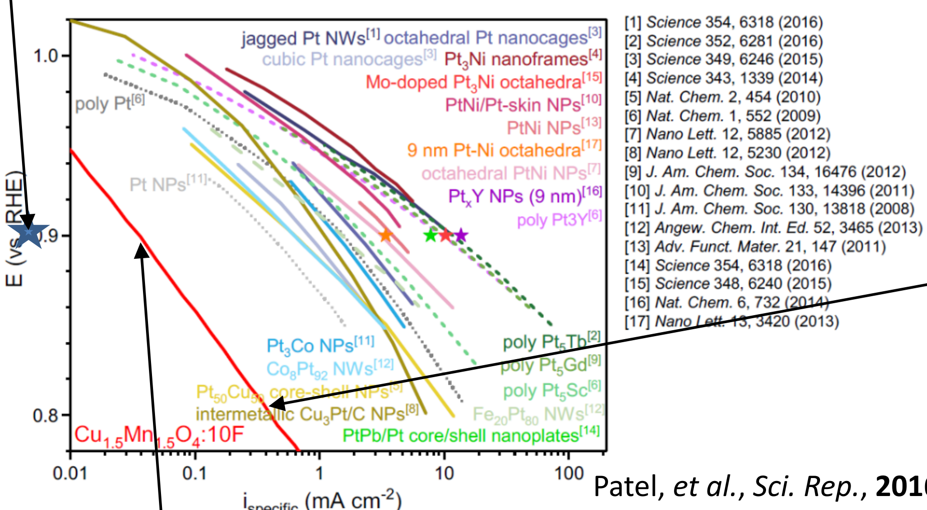
This year: MEA Fabrication and Performance Testing of initial ORR catalysts

- Catalyst layer composition optimization
  - Particle size of catalyst can be reduced to nanoparticles, but must study stability of particles at nano-scale



Seo, *et al.*, *Phys. Chem. Chem. Phys.*, **2012**, *16*, 895

Minimum performance for non-PGM electrocatalyst



Patel, *et al.*, *Sci. Rep.*, **2016**, *6*, 28367

1/10 performance of Pt is acceptable due to high electrode loading potential compared to 0.1 mg-cm^{-2} PGM

- Initial oxide ORR target for electrochemical testing identified
  - Reported activity is 10x the activity necessary to continue catalyst development
  - Additional parallel-path testing will explore doped $BaPbO_3$, FTO, TiO_x acid-(meta)stable phases

Any proposed future work is subject to change based on funding levels

Summary

United Technologies Research Center

- Discovery of acid-stable metal oxides with catalytically active elements has the potential for breakthrough ORR electrocatalytic performance
- Rapid computational and experimental approaches are being undertaken to discover dopant-stabilized metal oxides
- Identified acid-stable oxides will be subjected to high-throughput electrochemical testing to optimize electrocatalytic activity, ink/catalyst layer composition, and result in MEA testing
- This project will result in a greater understanding of how to enhance acid-stability of oxides

March 2019 Technical Target:

Demonstrate MEA with performance of 0.025 A-cm^{-2} at 0.9 V under 1 atm O_2 and 80 °C

March 2020 Technical Targets:

Target I.D. #	Characteristic	Units	2020 Targets
FC 4	Loss in initial catalytic activity	% mass loss	< 40
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Develop durable MEAs with PGM-free metal oxide ORR catalysts